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Citation: [AIP Conference Proceedings](#) **1805**, 040004 (2017); doi: 10.1063/1.4974425

View online: <https://doi.org/10.1063/1.4974425>

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High-Temperature Experimental and Thermodynamic Modelling Research on the Pyrometallurgical Processing of Copper

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Abstract. Uncertainty in the metal price and competition between producers mean that the daily operation of a smelter needs to target high recovery of valuable elements at low operating cost. Options for the improvement of the plant operation can be examined and decision making can be informed based on accurate information from laboratory experimentation coupled with predictions using advanced thermodynamic models. Integrated high-temperature experimental and thermodynamic modelling research on phase equilibria and thermodynamics of copper-containing systems have been undertaken at the Pyrometallurgy Innovation Centre (PYROSEARCH). The experimental phase equilibria studies involve high-temperature equilibration, rapid quenching and direct measurement of phase compositions using electron probe X-ray microanalysis (EPMA). The thermodynamic modelling deals with the development of accurate thermodynamic database built through critical evaluation of experimental data, selection of solution models, and optimization of models parameters. The database covers the Al-Ca-Cu-Fe-Mg-O-S-Si chemical system. The gas, slag, matte, liquid and solid metal phases, spinel solid solution as well as numerous solid oxide and sulphide phases are included. The database works within the FactSage software environment. Examples of phase equilibria data and thermodynamic models of selected systems, as well as possible implementation of the research outcomes to selected copper making processes are presented.

Keywords: pyrometallurgy, copper making, phase equilibria

INTRODUCTION

The majority of the world copper production from primary mineral sources and secondary recycling materials is carried out through pyrometallurgical processing routes. In 2015, there are at least 120 active copper smelters around the world ¹. More complex smelter feeds, tougher economic challenges and stricter environmental regulations mean that continuous improvement in the smelter is necessary for sustainable operation.

Even using existing assets, there are sometimes opportunities for improvement in the smelter day to day practice so as to achieve better valuable elements recovery and lower treatment cost. One possible approach to this matter is through the adjustment of slag chemistry. Slag composition can be modified in such a way that results in:

- (i) Lower copper losses.
- (ii) Lower liquidus temperature of slag, therefore decreasing operational temperature and saving energy costs.

Such improvements require detailed knowledge on the slag chemistry, including phase equilibria, thermodynamic and physicochemical properties of the systems.

Typical slag compositions from various copper making processes are summarized in FIGURE 1. The slag compositions used in the high-temperature copper making process range from fayalite slag ("FeO"-SiO₂), calcium ferrite slag (CaO-"Fe₂O₃"), or intermediate. Each slag system is unique and has different characteristics.

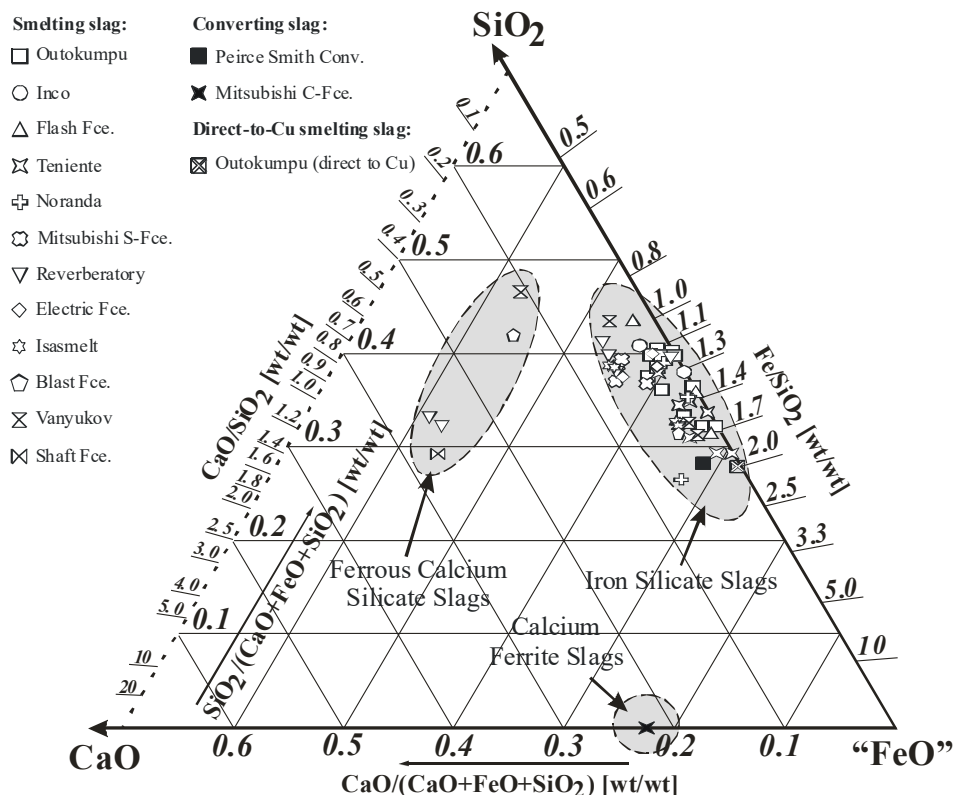


FIGURE 1. Typical slag compositions in copper making processes ²⁻⁵

Essential information on the chemistry of the copper-containing slags has been obtained at PYROSEARCH through an integrated controlled laboratory experiment and thermodynamic modelling research. The present article highlights the research findings on the phase equilibria determination and thermodynamic modelling of slag systems relevant to the copper making process, as well as their possible implementation to improve smelting practice.

HIGH-TEMPERATURE EXPERIMENTAL WORK

Phase equilibria of copper-containing slag systems are determined through the controlled laboratory equilibration of samples at high temperature, rapid quenching to retain compositions of phases in a sample, and measurement of compositions of the phases using the advanced analytical tool, Electron Probe X-ray Microanalysis - EPMA.

The sample is prepared from analytically pure powders, pre-sintered solids or pre-melted mixtures. The initial mixture of the sample is planned based on FactSage predictions or on previous experimental data. Al₂O₃ and MgO-based crucibles are avoided since they cause uncontrolled contamination of slag and solid phases by Al₂O₃ and MgO. To eliminate the problem, crucibles/substrates made of primary phase solids, such as spinel ("Fe₃O₄") and tridymite (SiO₂), are used.

Vertical tube furnaces are used to perform the equilibration. The furnace temperature is monitored by an alumina-shielded B-type thermocouple placed immediately adjacent to the sample. The overall temperature accuracy is estimated to be within 5 K or better. Equilibration is performed either in an inert atmosphere using argon or at controlled $P(O_2)$ atmosphere using CO/Ar/CO₂ gas flow. In recent years, the gas equilibration technique in PYROSEARCH has been further improved to enable accurate experiment with simultaneous control of $P(O_2)$ and $P(SO_2)$ ⁶.

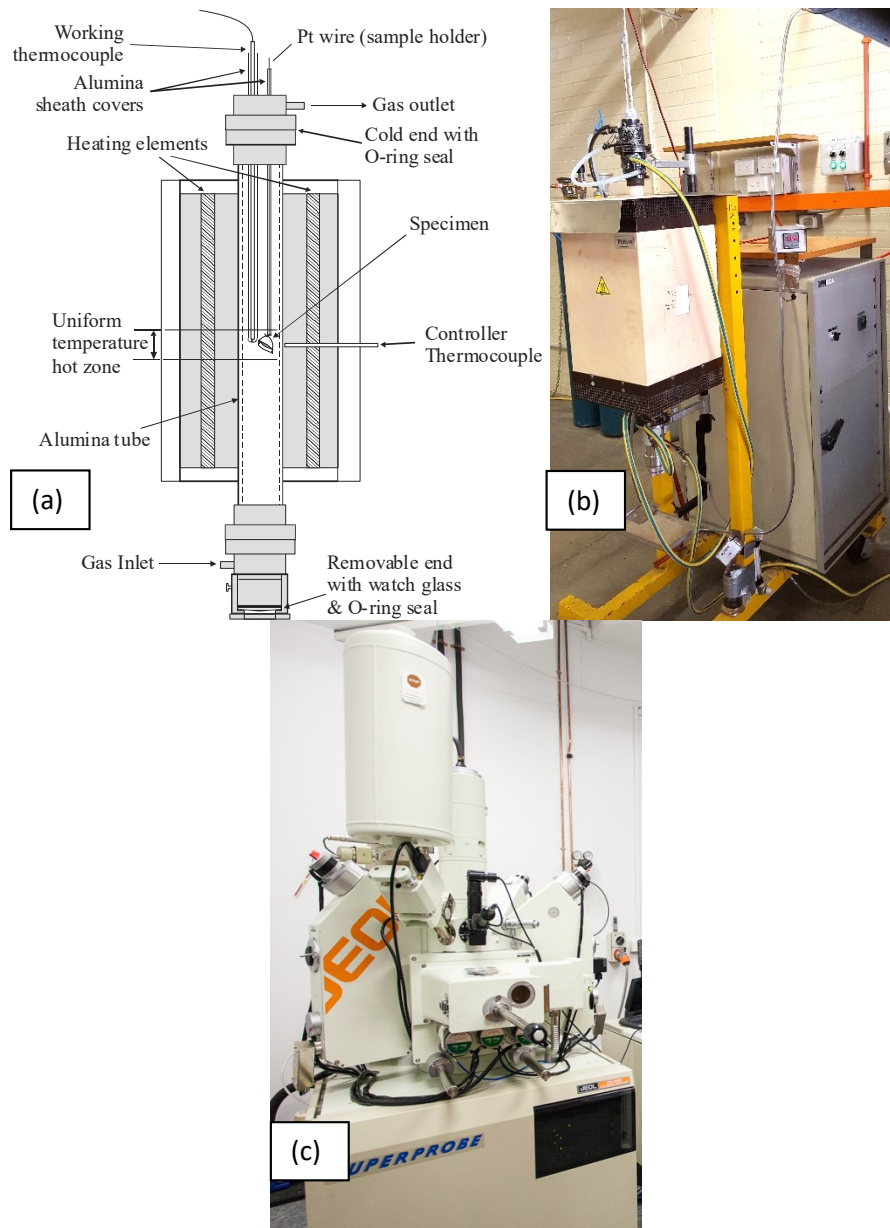


FIGURE 2. Facilities used in high-temperature equilibration research: (a) schematic of sample arrangement during equilibration in furnace, (b) vertical tube furnace, and (c) electron probe X-ray microanalyzer (JEOL JXA 8200L)

After equilibration for a specific time, the sample is quenched into cold water or brine solution so that the phases present at high temperature and their compositions are retained at room temperature. The quenched sample is then mounted, and polished. Initial examination of the sample is carried out using the optical microscopy and scanning electron microscopy (SEM) with energy dispersive detector (EDS) to visually identify phases formed after equilibration.

The compositions of the phases in the sample are measured using a JEOL JXA 8200L (trademark of Japan Electron Optics Ltd., Tokyo) electron probe X-ray microanalyzer (EPMA) with wavelength dispersive detectors (WDD). The EPMA enables the measurement of phases at high spatial resolution with accuracy within 1 wt % or better. Recently, laser ablation inductively coupled plasma mass spectrometry (LAICPMS) has been also utilized in the research activity. This advanced analytical tool has significantly lower detection limits which enable the research on minor elements distribution to be carried out on systems that were previously not accurately characterized ⁷.

FIGURE 2 shows main facilities used in the high-temperature equilibration research. The experimental technique and equipment have been used to accurately characterize high-temperature phase equilibria in various slag systems including CaO–“FeO”–SiO₂ system⁸⁻¹⁰, CaO–“FeO”–SiO₂–S system¹¹, CaO–“FeO”–SiO₂–MeOx (Me=Al, Mg) systems¹², “Cu₂O”–SiO₂–MeOx (Me=Al, Ca, Mg, Fe) systems^{13, 14}, “Cu₂O”–CaO–“Fe₂O₃” system¹⁵, “Cu₂O”–CaO–“FeO”–SiO₂ system^{16, 17}, and more.

THERMODYNAMIC DATABASE AND MODELLING

In the thermodynamic database development, all available thermodynamic and phase diagram data are evaluated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. This technique is often referred to as CALPHAD method in the literature. The results of the modelling are combined in a thermodynamic database, which can be used to simulate industrial processes^{18, 19}. Over the last decade, PYROSEARCH developed the most advanced and accurate thermodynamic database for pyrometallurgical copper production. Recent publications in thermodynamic modeling of the systems relevant to the pyrometallurgical copper extraction: Cu–O and Cu–O–S²⁰, Fe–O²¹, Fe–O–S²², Cu–Fe–O²³, Cu–Fe–O–S²⁴, Al–Fe–O²⁵, Ca–Fe–O²⁶, Fe–Si–O²⁷, Cu–Si–O, Cu–Ca–O, Cu–Ca–O–Si²⁸, Ca–Fe–Si–O²⁹. The results are summarized in two PhD theses^{30, 31}.

The most important phases in the pyrometallurgical production of copper are matte, metal, slag, spinel, numerous solid oxides, sulfides and sulfates, and gas. Liquid matte and metal are modeled as one merged solution (Cu^I, Cu^{II}, Fe^{II}, Fe^{III}, O, S), using the Modified Quasichemical Formalism in pair approximation^{32, 33}. The model covers the whole compositional range inside the Cu–Fe–O–S system from metals to oxides, to sulfides, to non-metals. The deviation from Cu₂S–FeS stoichiometry, observed in mattes is taken into account. The model describes a strong interaction between metals and nonmetals, which creates the short range ordering (SRO) between first nearest neighbors (FNN), affecting the entropy of mixing. The structure of slags is different from mattes. In addition to FNN SRO, slags exhibit second nearest neighbor (SNN) short range ordering between basic cations (Ca²⁺, Fe²⁺) and acidic cations (Si⁴⁺). In addition, sulphur is soluble in slags to a certain extent, and it plays an important role in the chemical solubility of copper in slag. To take these factors into account, the two-sublattice model within the Modified Quasichemical formalism in quadruplet approximation has been constructed: (Al³⁺, Ca²⁺, Cu¹⁺, Fe²⁺, Fe³⁺, Mg²⁺, Si⁴⁺)(O²⁻, S²⁻)³⁴. The very complex spinel solid solutions are described by the Compound Energy Formalism^{35, 36}: (Al³⁺, Cu²⁺, Fe²⁺, Fe³⁺, Mg²⁺)^{tetr}(Al³⁺, Ca²⁺, Cu²⁺, Fe²⁺, Fe³⁺, Mg²⁺, vacancy)₂^{oct}O₄²⁻. The Gibbs energies of charged end-members are expressed using linear combinations of Gibbs energies of real spinels and minimum of adjustable model parameters³⁰. Crystallographic data is used together with thermodynamic data. The gas phase is modelled as an ideal solution¹⁹.

RESULTS AND DISCUSSION

Copper making processes operate with complex Al–Ca–Cu–Fe–Mg–O–S–Si slag systems. To fully characterize and understand the chemistry of this multi-component system, experimental work and thermodynamic modelling of the phase equilibria of the slag system has to be carried out systematically starting from lower order systems and gradually progressing to higher order systems.

The current article gives examples of such approach showing previous systematic experimental investigation and thermodynamic modelling on several key sub-systems: Ca–Fe–O–Si, Al–Ca–Fe–O–Si, Ca–Fe–Mg–O–Si, Ca–Cu–Fe–O–Si, and Ca–Fe–O–S–Si. All of these sub-systems are within quaternary or more complex compositional space. FIGURE 3 shows schematic representations of the multi-component systems by projecting the phase equilibrium information onto the CaO–“FeO”–SiO₂ pseudo-ternary section. The representation of these complex systems into simpler forms leads to easier interpretation of the data.

FIGURE 4 (a) shows experimental determined liquidus composition in the CaO–“FeO”–SiO₂ system at 1300 °C and $P(\text{O}_2) = 10^{-8}$ atm⁹. The effect of Al₂O₃ and MgO on the liquidus is given in FIGURE 4 (b) and FIGURE 4 (c), respectively¹². The liquidus composition and copper solubility in the slag equilibrated with liquid copper are shown in FIGURE 4 (d)¹⁷. The liquidus composition and sulphur in the slag equilibrated system at 1300 °C, $P(\text{O}_2) = 10^{-8}$ atm, $P(\text{SO}_2) = 0.1$ atm are shown in FIGURE 4 (e)¹¹. The calculated liquidus composition and solubility of copper/sulphur using FactSage with an optimized database are also given in the figures. Although the absolute values of the experimental data are not entirely reproduced by the current model, the model still gives an accurate indication of the trend of the effect of different components on the slag liquidus and the effect of slag composition

on the solubility of copper/sulphur in slag. FIGURE 4 demonstrates that the current optimized model covers a wide range of slag compositions and is proven to be self-consistent throughout different sub-systems.

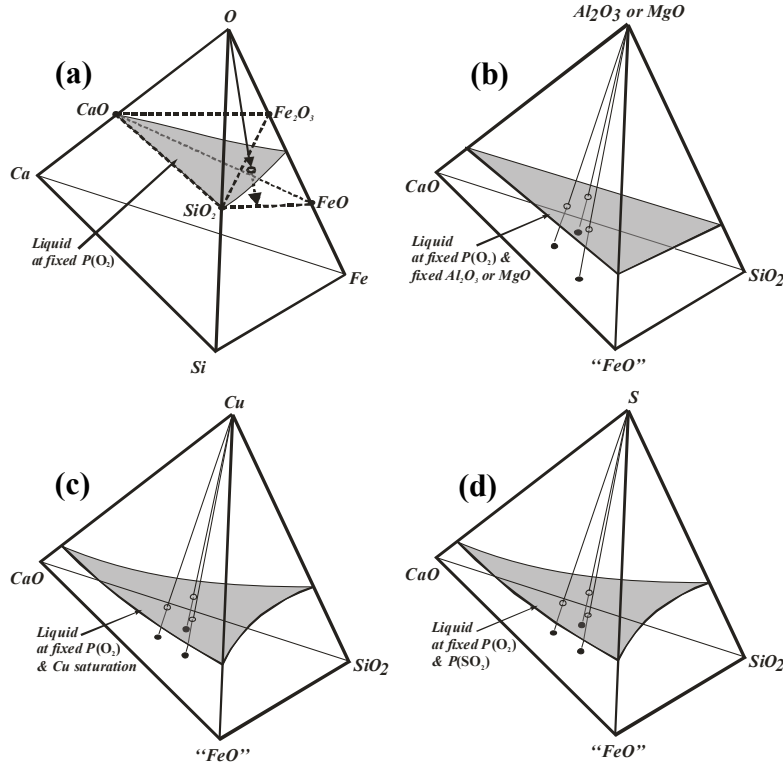


FIGURE 3. Compositional space of various slag systems projected onto CaO–‘FeO’–SiO₂ plane: (a) Ca-Fe-Si-O slag at fixed $P(\text{O}_2)$, (b) Al-Ca-Fe-Si-O or Mg-Ca-Fe-Si-O slag at fixed Al_2O_3 or MgO at fixed $P(\text{O}_2)$, (c) Cu-Ca-Fe-Si-O slag in equilibrium with liquid Cu at fixed $P(\text{O}_2)$, and (d) Ca-Fe-Si-O-S slag at fixed $P(\text{O}_2)$ and $P(\text{SO}_2)$

The optimized model can be used to predict the chemistry of slag at the composition and condition close to the actual industrial process. FIGURE 5 shows example of the application of the model for construction of fluxing diagram of slag in smelting process with matte grade = 60 wt% and $P(\text{SO}_2) = 0.25$ atm. The fluxing diagram is calculated for slag containing 4 wt% Al_2O_3 , 2 wt% CaO and 2 wt% MgO. The x-axis shows Fe/SiO₂ ratio in slag, which is an important fluxing parameter, and the y-axis shows slag temperature.

It can be observed that spinel (‘Fe₃O₄’) is stable at high Fe/SiO₂ region. With increasing Fe/SiO₂ in slag, the liquidus temperature of the spinel region increases from around 1150 °C at Fe/SiO₂ = 1.2 to approximately 1240 °C at Fe/SiO₂ = 2.0. Tridymite (SiO₂) is stable at Fe/SiO₂ below 1.1. In the tridymite area the liquidus temperature increases drastically with just a small decrease in Fe/SiO₂; the flexibility in Fe/SiO₂ ratio in slag in this area is therefore limited. In between the two region, pyroxene solid ((Ca,Mg,Fe)[Mg,Fe,Fe³⁺,Al]{Al,Fe³⁺,Si}SiO₆) is found to be stable.

The fluxing diagram in FIGURE 5 also provides information on the corresponding $P(\text{O}_2)$, Fe³⁺/Fe_{total}, Cu concentration in slag, S concentration in slag, S concentration in matte, and O concentration in matte. One of the interesting findings is given in FIGURE 5 (c) showing tridymite-saturated slag with lower copper solubility than that in spinel-saturated slag; this trend is the opposite from the trend observed in S-free system shown FIGURE 4 (d). It may appear to be a good option to operate in the low Fe/SiO₂ region to avoid high chemical copper loss into the slag. However, it should be realized that low Fe/SiO₂ in slag requires more silica fluxing, which means larger slag tonnage and possibly more viscous slag.

The application of the current thermodynamic database is not only limited to slag smelting process. It can also be used to different processes, such as copper converting, slag cleaning, high-temperature recycling, since the database has been optimized for wide range of compositions and conditions.

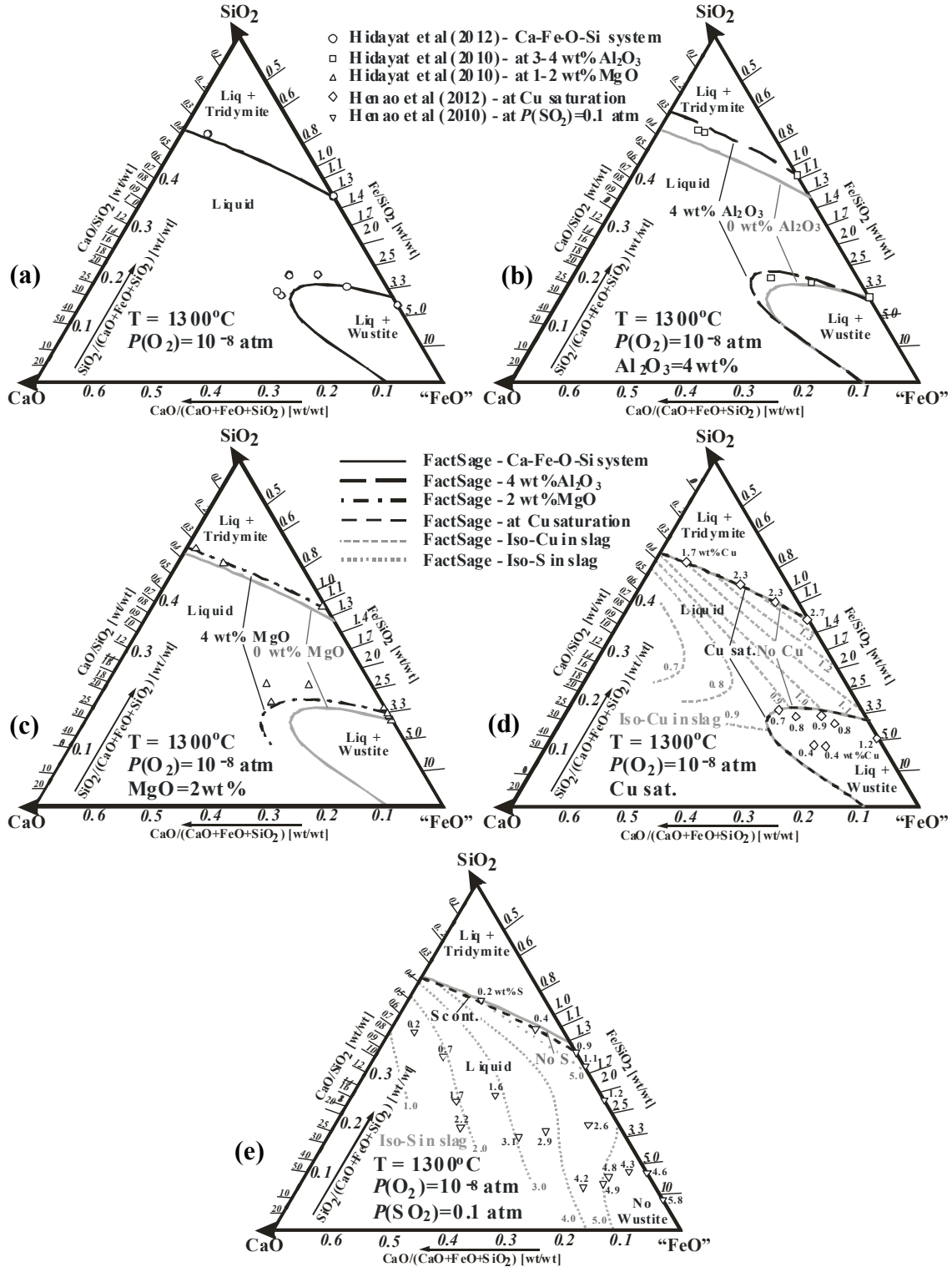


FIGURE 4. Experimental data and FactSage predictions with optimized database projected onto the CaO–“FeO”–SiO₂ plane, 1300 °C and $P(\text{O}_2) = 10^{-8}$ atm for: (a) liquidus composition in Ca-Fe-Si-O slag⁹, (b) liquidus composition in Al-Ca-Fe-Si-O slag at Al₂O₃ = 4 wt%¹², (c) liquidus composition in Mg-Ca-Fe-Si-O slag at MgO = 2 wt%¹², (d) liquidus composition and Cu solubility in Cu-Ca-Fe-Si-O slag in equilibrium with liquid Cu¹⁷, and (e) liquidus composition and S solubility in Ca-Fe-Si-O-S slag at $P(\text{SO}_2) = 0.1$ atm¹¹

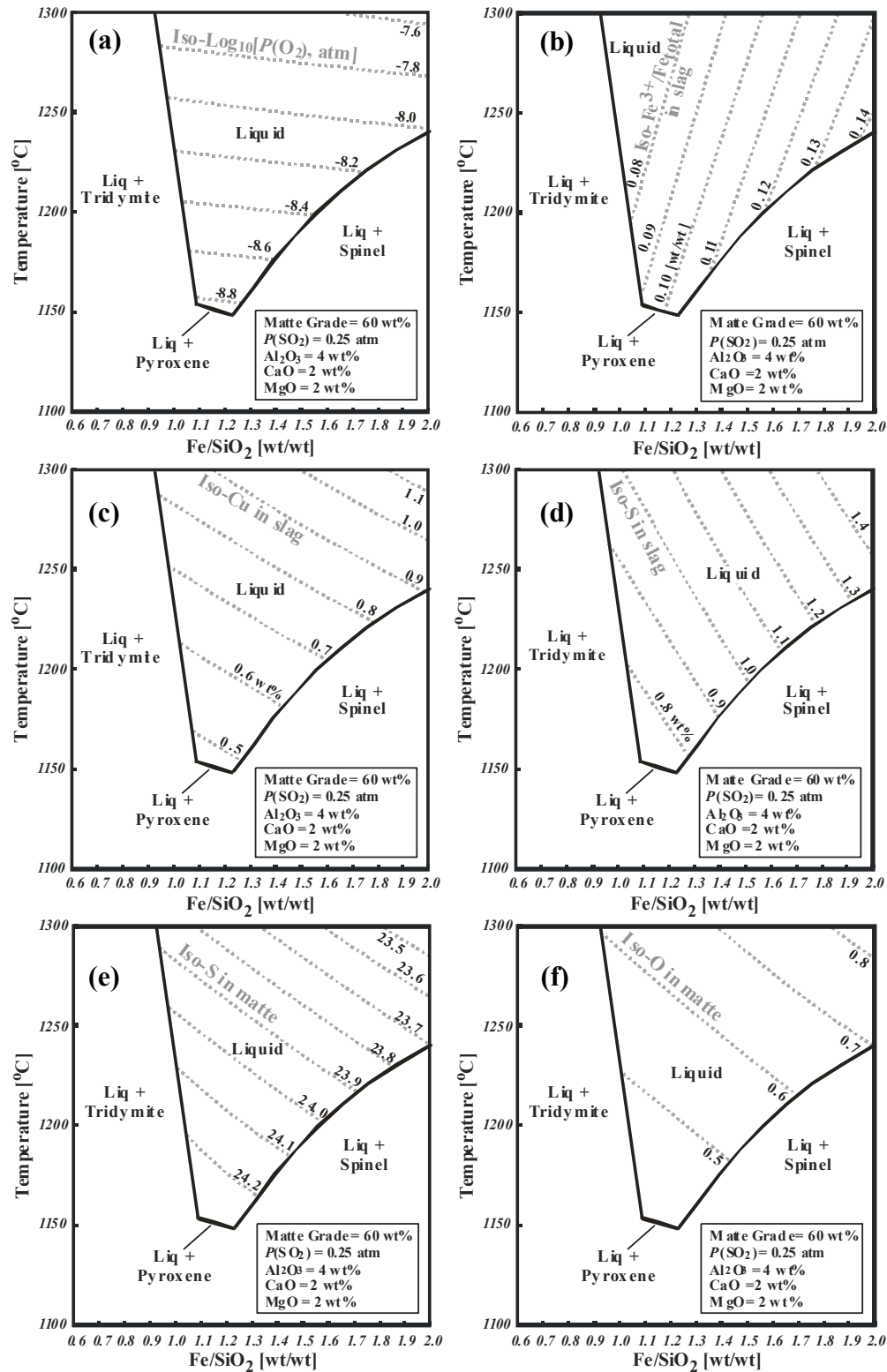


FIGURE 5. Fluxing diagrams predicted using FactSage with optimized database for Cu-Fe-Si-O-S-Al-Ca-Mg slag system at matte grade = 60 wt%, $P(\text{SO}_2) = 0.25 \text{ atm}$, $\text{Al}_2\text{O}_3 = 4 \text{ wt\%}$, $\text{CaO} = 2 \text{ wt\%}$ and $\text{MgO} = 2 \text{ wt\%}$, showing: (a) corresponding $\text{Log}_{10}[P(\text{O}_2), \text{atm}]$, (b) $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ in slag, (c) copper concentration in slag, (d) sulphur concentration in slag, (e) sulphur concentration in matte, and (f) oxygen concentration in matte

SUMMARY

Comprehensive research program combining high-temperature experimental and thermodynamic modelling on phase equilibria and thermodynamics of slag systems relevant to copper production have been carried out at PYROSEARCH. The experimental work involved high-temperature equilibration, rapid quenching and measurement using advanced analytical instrument. Optimized thermodynamic database of the Al-Ca-Cu-Fe-Mg-O-S-Si chemical system have been developed enabling the high temperature equilibria in complex, multi-phase copper making processes to be predicted using powerful computer based tools.

ACKNOWLEDGEMENTS

The research work reported in this article is from 1st – Copper consortium project. The authors would like to thank Australian Research Council Linkage program, Formerly: Xstrata Technology (Now: Glencore Technology), Formerly: Xstrata Copper (Now: Glencore), BHP Billiton Olympic Dam Operation, and Rio Tinto Kennecott Utah Copper, Corp., for their financial support for this research.

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